Figure 6-3. Mercury Concentrations (mg/kg) in Lake Michigan Surficial Sediments (1994-1996)

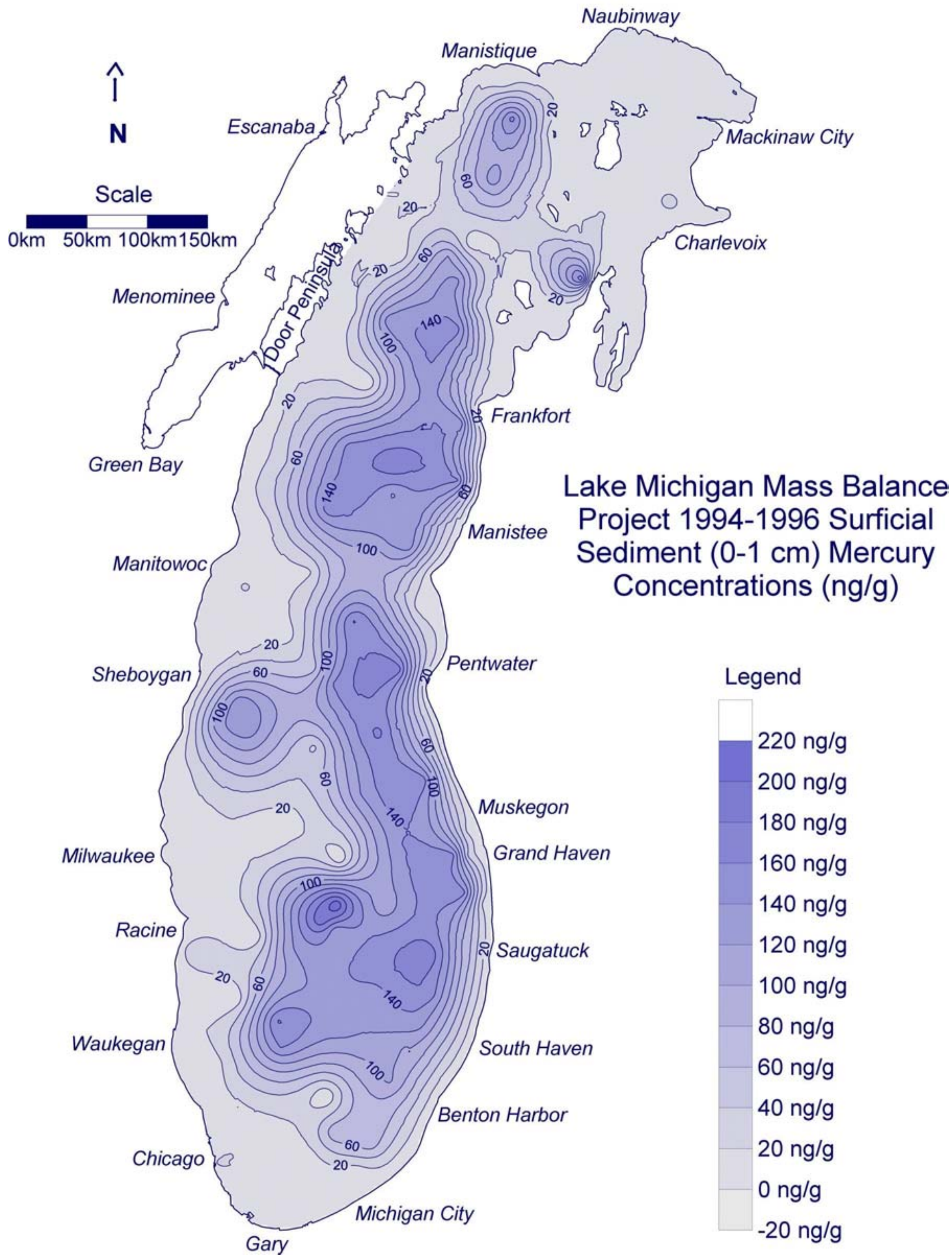


Figure 6-4. Lake Michigan Bathymetry with Depositional Basin Locations

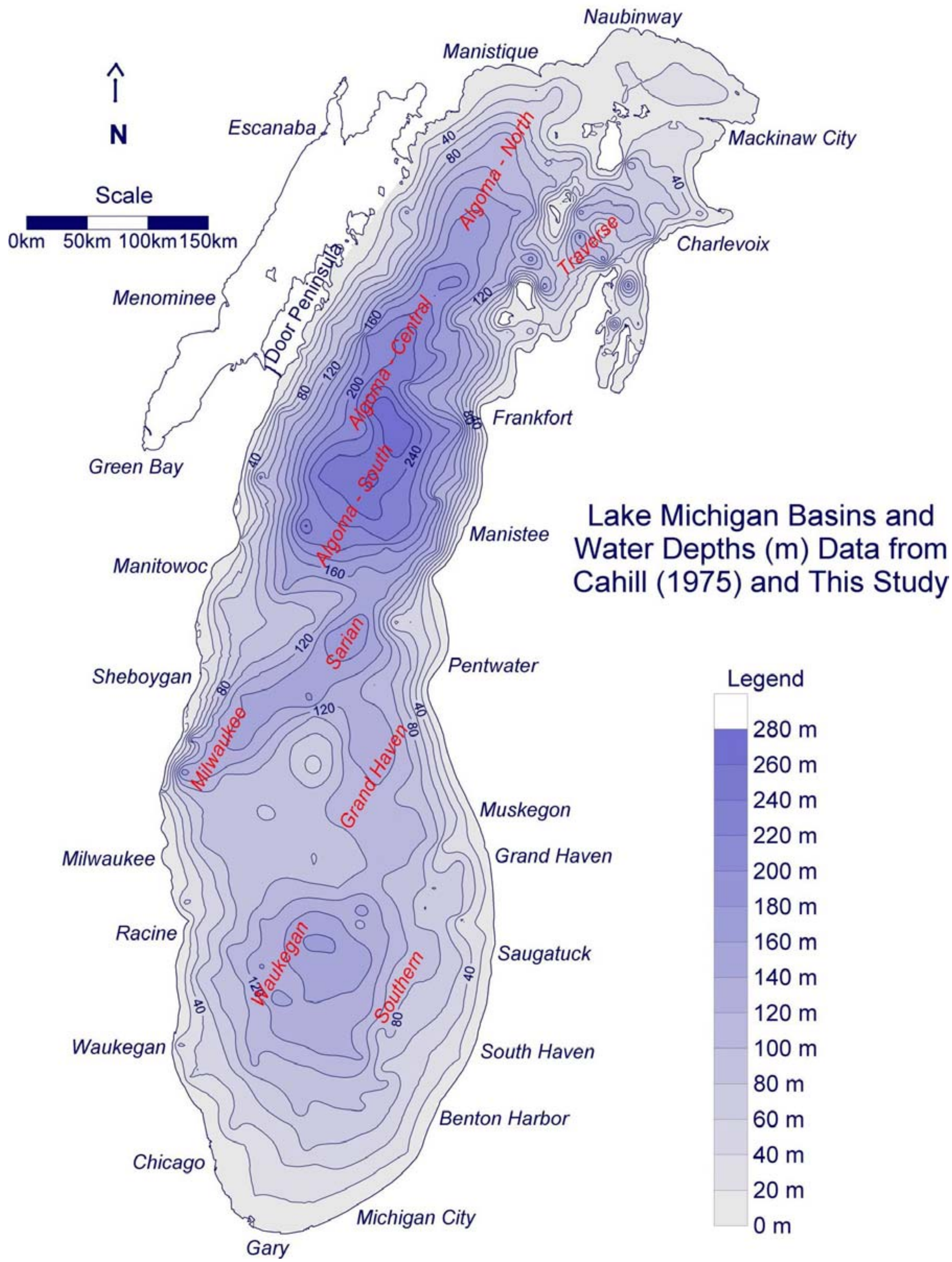
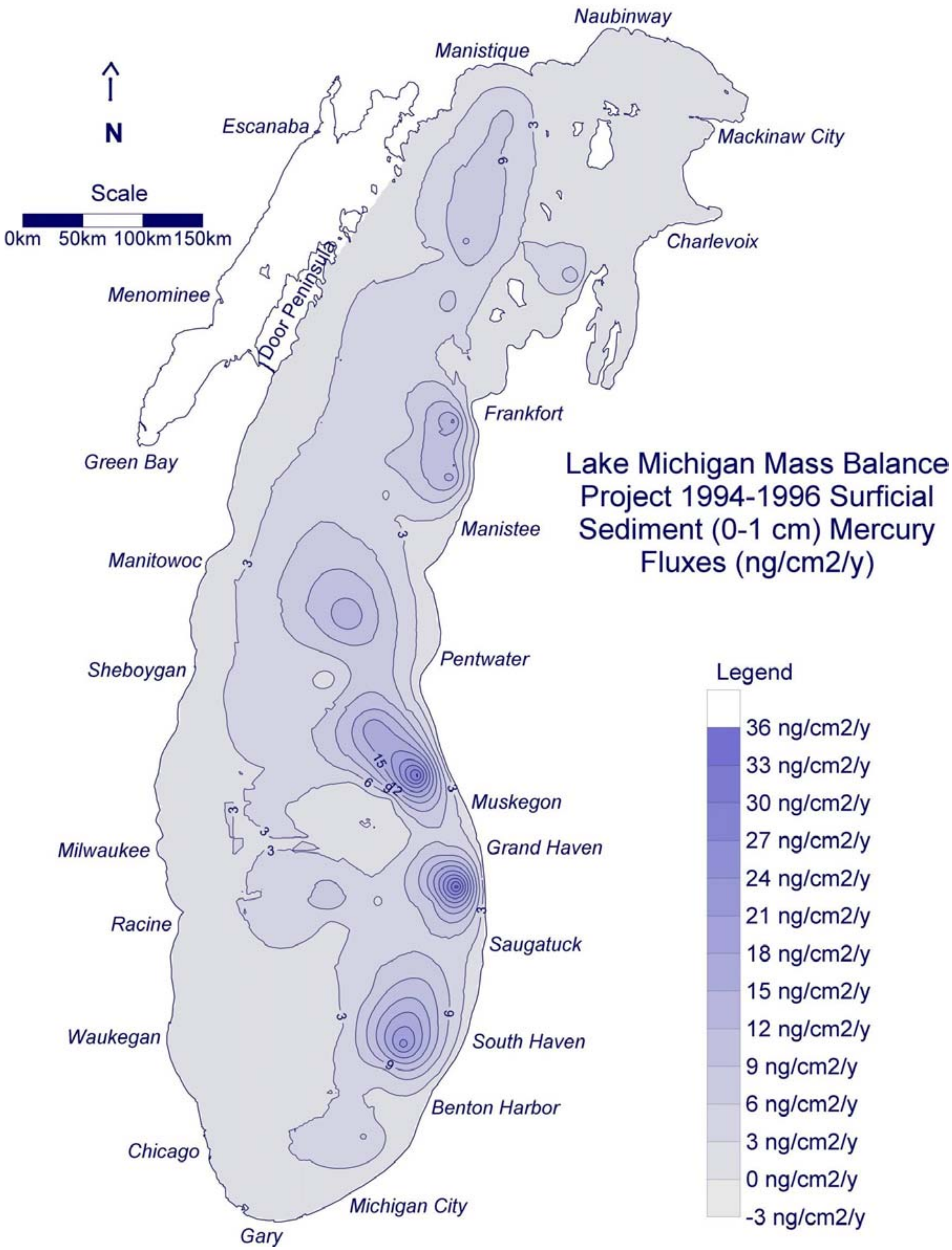


Figure 6-5. Mercury Fluxes (ng/cm²/y) to Lake Michigan Surficial Sediments (1994-1996)



6.3 Quality Assurance

As described in Section 1.5.5, the LMMB quality assurance program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the mercury monitoring portion of the study are further described in Section 2.6 and included use of SOPs, training of laboratory and field personnel, and establishment of measurement quality objectives (MQO) for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of data quality issues for the sediment mercury data is provided below.

As discussed in Section 6.1.2, the mass of resuspended sediment collected from the sediment traps was often too small to complete all analyses targeted in the LMMB Study. Because trap samples were collected and analyzed for mercury only during relatively high sediment flux periods, the mercury concentrations measured in sediment traps reflect those in resuspended sediments during these higher flux periods.

For some field and quality control (QC) samples, multiple analyses were conducted either on the field sample or the sample extract. Sample results were reported as average values of replicate results when available and are identified as average values in the Great Lakes Environmental Database (GLENDA) database. A standard reference material (SRM) from the National Institute of Standards and Technology (NIST) was included with sample batches to monitor performance of the analytical system. The Buffalo River Sediment, SRM 2704 (no longer available), has a certified value of 1.47 mg/kg. SRM samples were prepared and analyzed using the same extraction procedure as the field samples and were included with every group of samples extracted. Laboratory reagent blanks also were included with sample batches and were prepared and analyzed using the same extraction procedure as the samples. The mean mercury concentration measured in the blanks in a given batch was used to assess blank contamination in each sample. More than 80% of blanks were below the method detection limit (MDL).

Sediment samples were extracted using two different procedures. Most surficial sediments were extracted using a Leeman Labs, Inc. automated mercury system (Leeman Labs, Inc., 1993). All sediment trap samples and a few surficial sediment samples were extracted using a microwave digestion system (Uscinowicz and Rossmann, 1997). The Leeman automated extraction uses 50% aqua regia and potassium permanganate solutions and is more vigorous than the microwave extraction, which uses a 10% nitric acid solution. Mean recoveries of mercury in the NIST standard reference material samples were 97% for the automated digestion and 90% for the microwave digestion. This may be due, in part, to the smaller sediment sample mass that is used in the microwave digestion procedure compared to the automated digestion procedure, which requires as much as ten times the sample mass used in the microwave procedure. Also, the concentration of acid used in the extraction is greater for the automated extraction. Regardless of the extraction method, mercury concentrations measured in the SRM samples were within acceptance criteria for 100% of the sample analyses.

As discussed in Section 2.6, all data were verified by comparing the field and QC sample results produced by each principal investigator (PI) with their MQOs and with overall LMMB Study objectives. Field sample results were flagged when pertinent QC sample results did not meet acceptance criteria defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 6-9 provides a summary of flags applied to the sediment mercury data. The summary provided below includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6.

Table 6-9. Summary of Data Verification Flags Applied to Routine Field Sample Results for Sediment Mercury

Flag	Number of QC Samples	Percentage of Samples Flagged
EHT, Exceeded Holding Time	—	0
FBS, Failed Blank Sample	41 lab reagent blank samples	0
FDL, Failed Lab Duplicate	34 lab duplicate pairs	2% (4)
FFD, Failed Field Duplicate	4 field duplicate pairs	1% (2)
FSR, Failed Standard Reference Material	40 SRM samples	0
GTL, Greater than Operating Range	—	3% (5)
SCX, Suspected Contamination	—	2% (3)
UDL, Below Sample Specific Detection Limit	—	<1% (1)

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

All of the sediment samples were analyzed for mercury within the required holding time. Of the 41 laboratory reagent blank samples (LRBs) prepared and analyzed, none of the sample results exceeded the MQO and therefore, none of the routine field samples were flagged for a failed blank sample (FBS). Only 2% of the field sample results had associated laboratory duplicates with results above the maximum RPD/RSD of 15%, the acceptance criteria. The maximum RPD/RSD for these sample groups was 48%. Three percent of samples contained mercury concentrations that were greater than the operating range of the analytical system. These results are flagged in the database and should be considered estimated values. Two percent of the field samples were flagged for suspected contamination, based on laboratory notation that the samples were potentially contaminated during sample preparation and analysis in the laboratory. The laboratory notation is included in the database for these sample results in a comment field (exception to method text).

MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on three of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between the results for laboratory duplicate pairs. Table 6-10 provides a summary of data quality assessments for several of these attributes for the sediment mercury study data.

Table 6-10. Data Quality Assessment for Mercury in Sediment Samples

Parameter	Number of QC Samples	Assessment
Number of Routine Samples Analyzed	—	191
System Precision Mean Field Duplicate RPD (%), Samples $>MDL_S$	4 field duplicate pairs	38%
Analytical Precision Mean Lab Duplicate RPD (%), Samples $>MDL_S$	30 lab duplicate pairs	8.5%
Analytical Bias, Mean SRM[3] (%)	40 SRM samples	92%
Analytical Sensitivity, Samples reported as $<MDL_S$ (%)	—	0.5%

MDLs = Sample Specific Detection Limit
SRM = Standard Reference Material, Buffalo River Sediment, SRM 2704 (NIST 1990)

System precision, estimated as the mean relative percent difference for field duplicates, was 38%. However, because only four field duplicates were collected and analyzed, this estimate may not accurately reflect the variability associated with sampling and analytical activities. Analytical precision, estimated as the mean relative percent deviation for laboratory duplicates, was much lower, at 8.5%, suggesting that either the small number of field duplicates did not accurately reflect the variability associated with sampling and analytical activities, or the variability associated with sampling is much greater than that associated with the analytical activities. This latter possibility is not unexpected for sediment sampling. Analytical bias, estimated as the mean recovery of standard reference materials, was 92%, which indicates a slight low bias in the analytical results. More than 99% of samples contained mercury concentrations above the detection limit.

6.4 Data Interpretation

Lake Michigan surficial sediments have elevated mercury concentrations compared to pre-settlement concentrations. Fluxes of mercury to the lake from atmospheric, tributary, and shoreline sources are redistributed within the lake by wave action and current transport. This leads to a definitive distribution pattern of mercury concentrations in Lake Michigan sediments and fluxes to those sediments. Only the mercury results for surficial sediment are discussed in this chapter. A discussion of moisture content is not included in this chapter.

6.4.1 Comparison to Other Great Lakes Sediments

Excluding Green Bay, Lake Michigan surficial sediments have relatively low mercury concentrations (Table 6-11).

Table 6-11. Comparison of Lake Michigan Surficial Sediment Mercury Concentrations to those at other Locations in the Great Lakes Basin

Location and Years	N	Mean (ng/g)	Standard Deviation (ng/g)	Median (ng/g)	Minimum (ng/g)	Maximum (ng/g)	Reference and Surficial Interval Sampled
Green Bay 1987 - 1990	74	360	270	280	6	1100	Rossmann and Edgington (2000) 0-1 cm
Superior 1983	31	180	180	140	27	960	Rossmann (1999) 0-2 cm
North Channel 1973	55	150	230	NA	8	1100	Thomas (1974) 0-3 cm
Georgian Bay 1973	117	260	1000	NA	12	9500	Thomas (1974) 0-3 cm
Huron 1969	163	220	160	NA	54	800	Thomas (1974) 0-3 cm
St. Clair 1970	55	630	630	NA	70	2600	Thomas (1974) 0-3 cm
Erie 1971	243	610	700	NA	13	7500	Thomas (1974) 0-3 cm
Ontario 1968	248	650	510	NA	32	2100	Thomas (1974) 0-3 cm
Michigan 1994 - 1996	118	78	65	73	2	260	Rossmann (this study) 0-1 cm

NA = Not applicable

In the main basin of Lake Michigan, mean mercury concentration is nearly one-half of those found in all the other Great Lakes, making the lake relatively uncontaminated with mercury. However, it should be noted that Lake Michigan sediments are being compared to much earlier results for other locations. Contamination of sediments was historically higher than at present. It should also be noted that the surficial sediment intervals compared are different in thickness and represent different periods of time that are integrated to produce the mercury concentration reported for the homogenized layer of sediment. Due to the difference in sampling year and sediment thickness, cautions should be used when comparing LMMB data to these other studies. Recent data having similar time intervals represented by the top interval are insufficient to be representative of Lakes Superior, Huron, Erie, and St. Clair sediments.

Note should be made of the fact that Green Bay, a bay of Lake Michigan, has sediments that are contaminated with mercury relative to other Great Lakes locations. The contamination of these sediments has been attributed to historical industrial practices in the Fox River drainage basin (Rossmann and Edgington, 2000).

6.4.2 Comparison to Historical Lake Michigan Concentrations

For Lake Michigan, several historic data sets exist for mercury in surficial sediments (Table 6-12). Kennedy *et al.* (1971) reported on mercury concentrations in the 0-1 and 0-5 cm intervals of surficial sediments collected during 1969 and perhaps 1970. Samples were collected from the southern basin of Lake Michigan from 31 sites (Figure 6-6). A much more comprehensive collection was made in 1975 and reported in Cahill (1981). The surficial 3 cm of sediment were collected from 254 locations from all basins of the lake (Figure 6-7). Mercury results are available for one of three sediment cores collected from southern Lake Michigan in 1981 (Figure 6-8). Results for the LM-81-HS core are reported by Pirrone *et al.* (1998). Additional details for that core are reported here.

Table 6-12. Comparison of Current Lake Michigan Results to Historical Data

Years Collected	N	Mean (ng/g)	Standard Deviation (ng/g)	Median (ng/g)	Minimum (ng/g)	Maximum (ng/g)	Reference and Surficial Interval Sampled
1969-1970?	31	150	100	120	30	380	Kennedy *et al.* (1971) surficial 0-1 through 0-5 cm
1975	254	110	110	60	20	670	Cahill (1981) 0-3 cm
1981	1	200	—	—	—	—	Pirrone *et al.* (1998) 0.5 cm
1994-1996	118	78	65	73	2	260	Rossmann (this study) 0-1 cm